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New Type of π-Conjugated Polymers Constituted of Quinone Units in the Main Chain

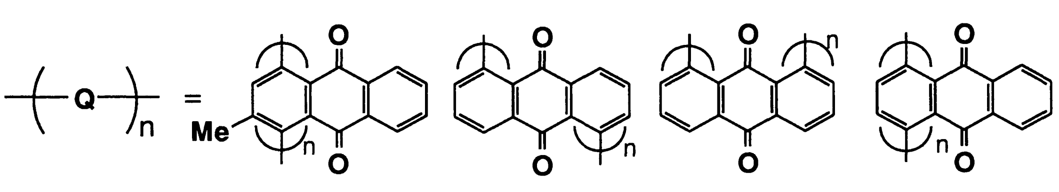
Hideki ETORI, Takaki KANBARA, and Takakazu YAMAMOTO*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

New π-conjugated polymers having quinone units as the recurring units, e.g., poly(2–methyl–9,10–anthraquinone–1,4–diyl) P(Me–1,4–AQ) with molecular weight of 56000, have been prepared by dehalogenation polycondensation of dichloroquinones. P(Me–1,4–AQ) exhibits unique redox behaviors due to electronic interactions between the multiple redox centers in the polymer through the π–conjugated system.

Various types of π–conjugated polymers have been reported, and their redox (or p and n doping) behaviors as well as conducting behaviors of oxidized or reduced polymers have been reported. However, π–conjugated polymer constituted of recurring quinone units, one of the most basic redox–active functional units, has received much less attention presumably due to difficulty to prepare such polymers by usual methods.

We have applied the previously reported dehalogenation polycondensation of the dihalogenated aromatic compounds using zero valent nickel complex$^{1)}$ to dichloroquinones to prepare such polymers, and now report redox behaviors of the poly(quinone)s obtained: poly(2–methyl–9,10–anthraquinone–1,4–diyl) P(Me–1,4–AQ), poly(9,10–anthraquinone–1,5–diyl) P(1,5–AQ), poly(9,10–anthraquinone–1,8–diyl) P(1,8–AQ), and poly(9,10–anthraquinone–1,4–diyl) P(1,4–AQ).

$$\mathrm{Cl{-}Q{-}Cl} \xrightarrow[\text{DMF} \quad 60\ ^\circ\text{C} \quad 48\ \text{h}]{\text{Ni(cod)}_2 \quad \text{bpy}} \left(\!-\mathrm{Q}-\!\right)_n \tag{1}$$



P(Me–1,4–AQ) P(1,5–AQ) P(1,8–AQ) P(1,4–AQ)

The corresponding monomers, dichloroquinones, were prepared according to reported methods.$^{2)}$ Each monomer (1.33 mmol) was added to an N,N–dimethylformamide DMF solution (15 cm^3) containing bis(1,5–cyclooctadiene)nickel Ni(cod)$_2$ (440 mg, 1.60 mmol), 1,5–cyclooctadiene (140 mg, 1.33 mmol), and 2,2'–bipyridine bpy (250 mg, 1.59 mmol) under inert gas and the reaction mixture was stirred at 60 °C for 48 h. The obtained polymer was worked up in a manner similar to that applied for isolation of poly(arylene) prepared by similar dehalogenation polymerization.$^{1)}$ Yellow P(Me–1,4–AQ) was obtained in 89% yield and its analytical data (Found: C, 82.6; H, 3.4; Cl, 0%. Calcd. for $(C_{15}H_8O_2)_n$: C, 81.8; H, 3.7%) agreed with the structure shown in Eq. 1.

P(Me–1,4–AQ) is soluble in $CHCl_3$ (about 10 mg / 1 cm^3), 1–methyl–2–pyrrolidinone NMP and CH_2Cl_2, and its IR spectrum (Fig. 1a) as well as ^1H-NMR spectrum (90 MHz, $CDCl_3$: δ: 2.1, 2.3 and 2.6 ppm (CH_3 of head–to–tail and head–to–head units, singlets, 3H), 7.5-8.3 ppm (multiplet, 5H)) are reasonable for the structure. P(Me–1,4–AQ) has molecular weight of 56000 as determined by light scattering method in $CHCl_3$. Use of other dichloroquinones gives the corresponding poly(quinone)s shown in Eq. 1; their IR spectra (Fig. 1) are reasonable and analytical data roughly agree with their structures. However, they show considerably lower solubility than P(Me-1,4-AQ).

Redox behaviors of P(Me–1,4–AQ) have been investigated by cyclic voltammetry CV by using a cast film laid on Pt plate and the comparison of its CV curve with that of 2–methyl–9,10–anthraquinone is show in Fig. 2. The CV curve of P(Me–1,4–AQ) is essentially unvaried in repeated scans. CV curves of quinones usually show two redox cycles due to Wurster–type two step redox reactions$^{3)}$ (quinone / radical anion couple and radical anion / dianion couple) as shown in Fig. 2c, and Eqs. 2 and 3.

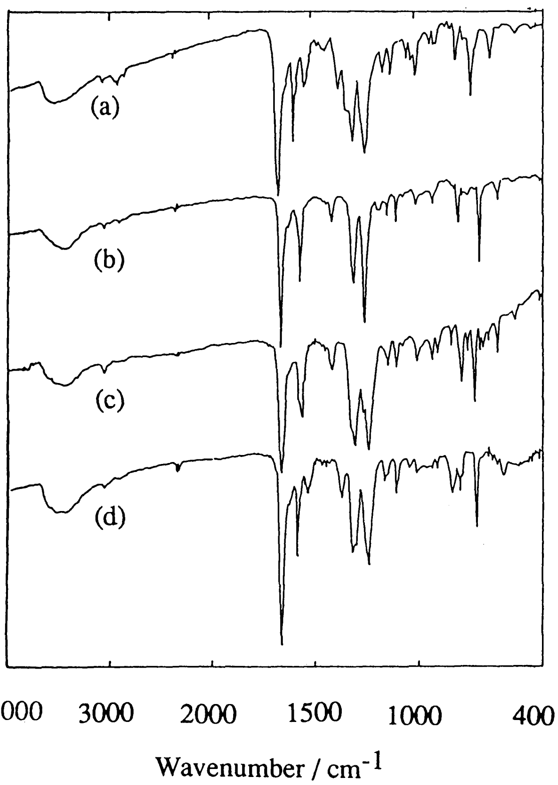


Fig. 1. IR spectra of (a) P(Me–1,4–AQ), (b) P(1,5–AQ), (c) P(1,8–AQ), and (d) P(1,4–AQ).

In the case of P(Me–1,4–AQ), the reduced molecules contain the neutral, radical anion, and dianion units (Eqs. 4 and 5) in the same molecule, and these units are considered to exchange electron(s) between them through the π–conjugated system; electron(s) in these units are considered to be delocalized in the polymer chain. Broadening of the first (E°_1) and second (E°_2) CV cycles of P(Me–1,4–AQ) (Figs. 2a and 2b) compared with those of 2–methyl–9,10–anthraquinone (Fig. 2c) as well as smaller potential difference (0.31 V; Fig. 2a, Fig. 2b, and Eqs. 4 and 5) between E°_1 and E°_2 compared with that (0.57 V; Fig. 2c and Eqs. 2 and 3) of 2–methyl–9,10–anthraquinone seem to be attributable to the occurrence of such electron exchange. Preparation of non–π–conjugated poly(quinone)s having quinone units as pendant group and their CV data have been reported.$^{4)}$ However, in cases of these polymers, such broadening of the CV cycles as that described above does not take place.$^{4)}$

Doping levels for Eq. 4, x/n, and Eq. 5, y/n, estimated from area of the two redox cycles shown in Fig. 2a are 0.62 and 0.48, respectively, and the smaller y/n value than the x/n value indicates that extensive electrochemical reduction to form the dianion unit (Eq. 5) is more difficult than the first reduction (Eq. 4), due to the presence of many negatively charged anion and dianion centers in the same π–conjugated polymer chain. However, in the case of monomeric anthraquinone, the second reduction (Eq. 3) occurres normally as revealed by an equal area of the two redox cycles of the monomeric anthraquinone (Fig. 2c).

At the scanning rate of 20 through 100 mVs^{-1}, CV curves essentially with the same shape are observed. On the other hand, when the scanning rate is slowered from 20 mVs^{-1} (Fig. 2a) to 10 mVs^{-1} (Fig. 2b), a new reduction peak appears at about -1.88 V although its corresponding oxidation peak is not clearly observed presumably due to overlapping with the E°_2 cycle. The observation of the reduction at -1.88 V only at the slow scanning rate suggests that there is a slow electrochemical step for further extra reduction of the anion radical species in Product–2 formed in Eq. 5.

Reduction of yellow P(Me–1,4–AQ) causes color changes as shown in Eqs. 4 and 5, and the color change has been followed spectroscopically. UV–vis spectrum of P(Me–1,4–AQ) film laid on indium–tin–oxide ITO glass substrate by casting from $CHCl_3$ exhibits a relatively sharp π–π* absorption band at 376 nm, which is shifted to a longer wavelength by about 50 nm from that of 2–methyl–9,10–anthraquinone (λmax = 329 nm). Reduction of the P(Me–1,4–AQ) film at -1.5 – -1.7 V vs. Ag/Ag^+ in a CH_3CN solution of $[NEt_4][ClO_4]$ gives rise to new absorption bands at 460, 560, 920, and 1040 nm assignable to overlapped peaks of the radical anion (560, 920, and 1040 nm) and dianion (460 and 550 nm); these peaks are also shifted from those of monomeric radical anion $AQ^{\bullet -}$ (488, 776, and 866 nm)[5] and dianion AQ^{2-} (417 and 508 nm).[5] At more negative potential of -2.0 V vs. Ag/Ag^+, intensities of the peaks at 460 and 550 nm increase whereas those at 920 and 1040 nm decrease in accord with the occurrence of the electrochemical reaction expressed by Eq. 5.

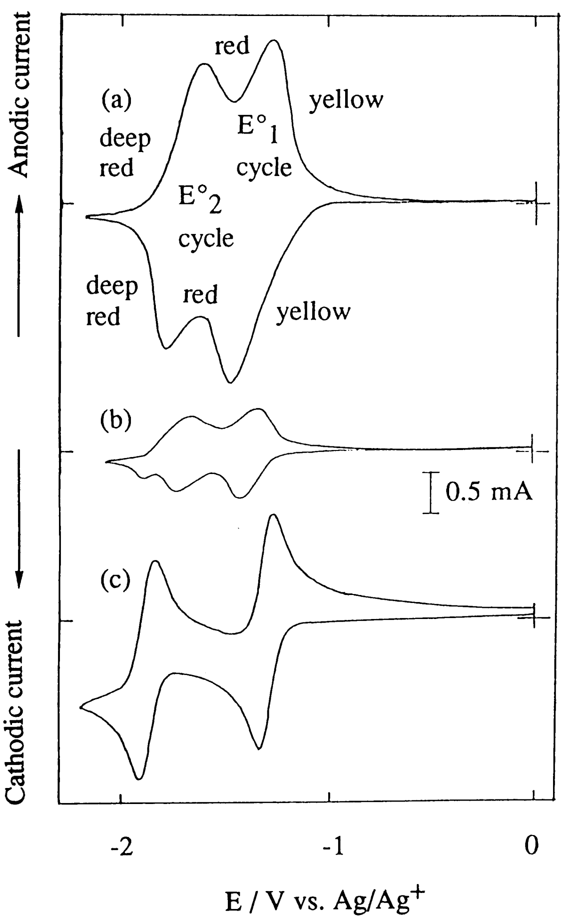
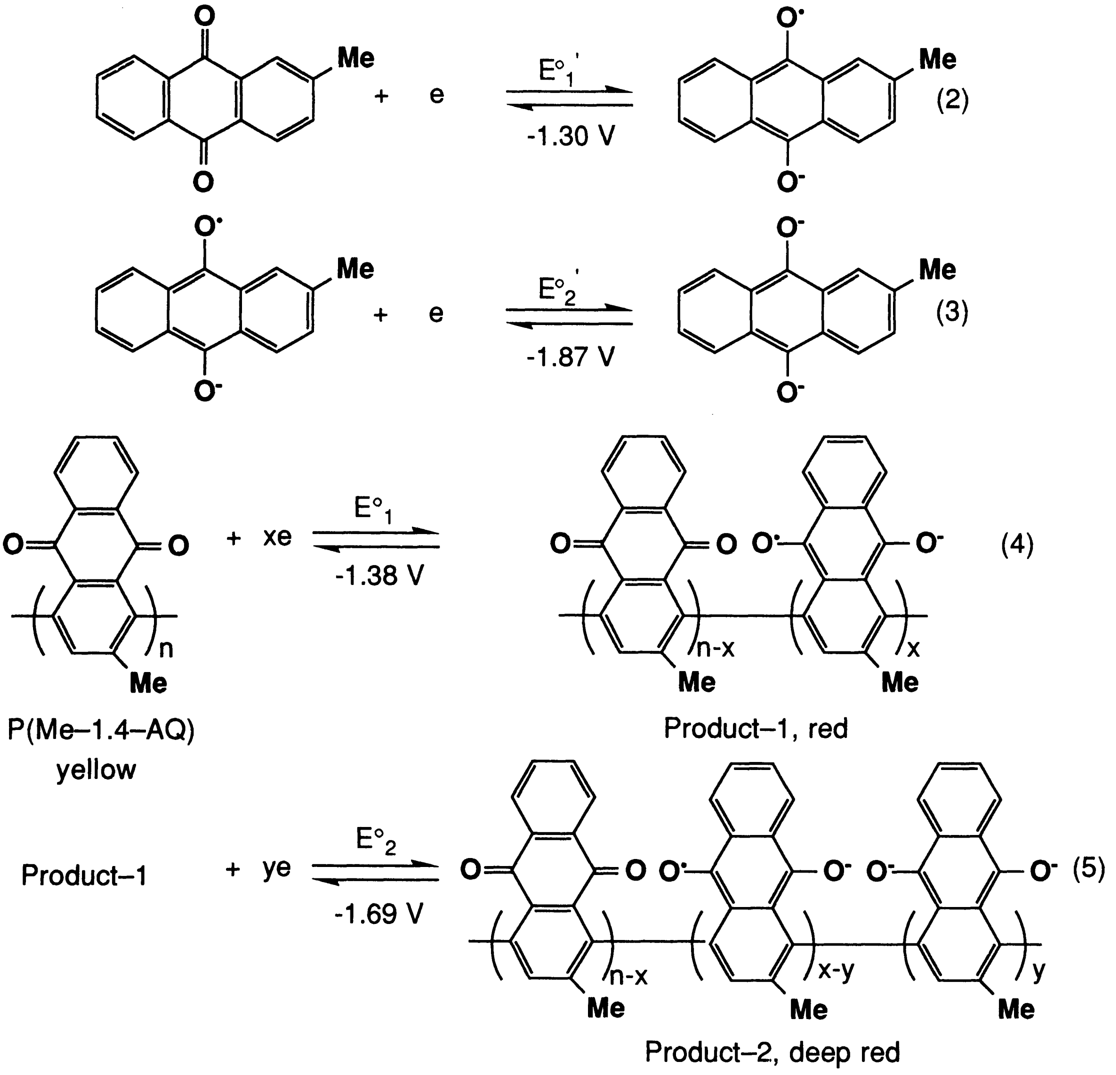


Fig. 2. CV curves of P(Me–1,4–AQ) laid on Pt plate in a CH_3CN solution of 0.1 M $[Et_4N][ClO_4]$ at scanning rate of (a) 20 mVs^{-1} and (b) 10 mVs^{-1}, respectively, and (c) that of 2 x 10^{-3} M 2–methyl–9,10–anthraquinone in a CH_3CN solution of 0.1 M $[Et_4N][ClO_4]$ at scanning rate of 100 mVs^{-1}.

Chemical reduction of P(Me–1,4–AQ) with N_2H_4 in a homogeneous system in NMP gives somewhat different change in the UV spectrum from that observed with the above polymer film, leading to rise of peaks at 380, 469, 580, 748 nm. P(Me–1,4–AQ) and other poly(9,10–anthraquinone)s show electrical conductivities (σ) of about 10^{-8} Scm^{-1}, whereas sodium doping of these polymers with



The same $E°_1$ and $E°_2$ values were obtained from both Figs. 2a and 2b.

excess sodium naphthalide in THF gives black doped polymers which exhibit the σ values of an order of 10^{-5} Scm^{-1} (e.g., 1.8×10^{-5} Scm^{-1} for P(Me–1,4–AQ)) as measured with compressed powders.

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